THE REFLECTION OF LITHIUM IONS FROM METAL SURFACES

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

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RAYMOND BURKERT SAWYER

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THE REFLECTION OF LITHIUM IONS FROM METAL SURFACES

By R. B. Sawyer

Ryerson Physical Laboratory, University of Chicago

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Abstract

A study has been made of the reflection of lithium ions from reflectors of platinum foil and of nickel crystals deposited on tungsten foil. Movable ground joints in the tube were completely eliminated in order to prevent contamination of the reflector surfaces by grease. Readings were taken with both cold and hot reflectors. Spodumene was used as a source of ions and reflection was studied in the meridian plane only.

Superposed on a diffuse scattering of ions were two reflected beams. One was reflected nearly specularly, as found by Read and by Gurney, the angle of maximum reflection, however, being independent of accelerating potential. The other beam appeared only at voltages above 200 and was composed of ions most of which had retained 80 percent or more of their original energy. This beam was found between the incident beam and the normal to the surface, at angles independent of the accelerating potential up to 700 volts. This independence of angle on voltage forbids diffraction interpretations. A tentative explanation consists in supposing specular reflection from the (110) planes of the nickel crystals, but the agreement is not entirely satisfactory.

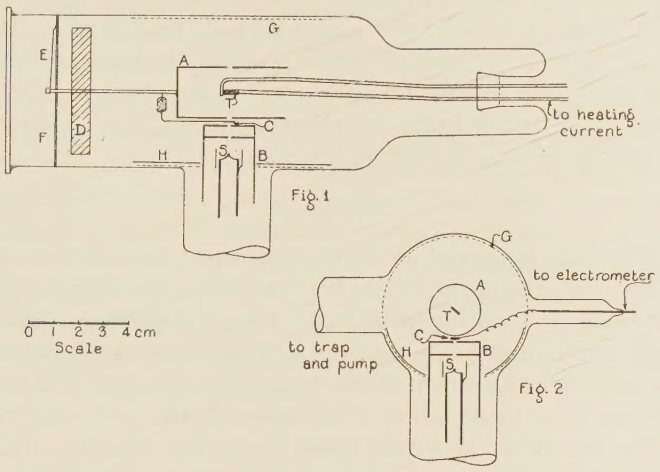
THE reflection of lithium and potassium ions from a platinum surface has been investigated by Read,[1] and that of lithium, potassium, and caesium from platinum by Gurney.[2] Both found considerable reflection from a clean platinum surface, the maximum occurring at an angle somewhat larger than that corresponding to specular reflection. Since an extremely clean reflector seemed to be necessary in order to obtain appreciable reflection, it was desirable to continue the study, making every effort to avoid contamination of the reflector, especially by grease vapor. The discovery of electron diffraction by crystals[3] and the work of Ellett and Olson[4] on reflection of neutral atoms by crystals suggested a trial of crystal surfaces as reflectors of positive ions.

Apparatus

The tube used is shown in Fig. 1 and Fig. 2. A tiny crystal of spodumene, S, on an electrically heated platinum strip was used as a source of lithium ions.[5] These were accelerated to the drum, B, and a portion passed through holes 1 mm in diameter, and entered the cylinder, A, which had a 3 mm slot cut around it to admit them. After striking the reflector, T, those ions which

[1] Read, Phys. Rev. **31**, 629, (1928).
[2] Gurney, Phys. Rev. **32**, 467 (1928).
[3] Davisson and Germer, Phys. Rev. **30**, 705 (1927).
[4] Ellett and Olson, Phys. Rev. **31**, 643 (1928).
[5] Read, reference 1, p. 629.

were reflected at any given angle could be caught by the collector, C, which was a 2 mm$\times$7 mm nickel strip rigidly fastened by means of a Pyrex bead to the axis of the cylinder, A. The collector-cylinder system was mounted in a supporting framework (not shown in the figure) so that it could be rotated from the outside of the tube by an electromagnet applied to the soft iron armature, D. The angle at which the collector was set was indicated by a pointer, E, moving over a graduated circle, F. The collector was connected to a string electrometer by a flexible lead. The positive ion current from the collector was balanced by a negative current from an ionization chamber.[6] The central part of the tube was shielded by a gauze, G, and an additional screen, H, of sheet metal was placed around the bottom part of the tube in order to prevent the escape of any positive ions from the source except



Figs. 1, 2. Construction of tube.

through the holes in the top of the drum, B. The cylinder and framework supporting it were grounded through the same lead as the screen, H, but the gauze, G, had a separate ground connection. Neither of these ground leads is shown in the figure. Tungsten wires were used for sealing through the Pyrex.

The reflector was either a 5/16 in.$\times$3/8 in. strip of platinum-iridium foil (10 percent iridium) 0.0005 in. thick, or a 1/8 in.$\times$3/8 in. strip of tungsten foil, kindly supplied Dr. W. E. Forsythe, upon which nickel crystals had been deposited by evaporation, according to the method of Rupp.[7] He states that the minute crystals so formed are oriented with their (111) planes parallel to the surface of the backing foil. The platinum foil was mounted so as to be kept always under slight tension by a tungsten spring, while the heavy nickel wires supporting the nickel crystal reflector had enough elasticity to keep the tungsten foil taut. In either case the reflector could be heated electrically to any temperature desired. Except as otherwise noted, all metal parts were made of nickel.

[6] Read, reference 1, p. 630.

[7] Rupp, Ann. d. Physik **1**, 801 (1929).

Spodumene proved to be so satisfactory a source of lithium ions that the stem supporting the source and drum was sealed permanently into the side tube. A useful life of from 75 to 100 hours for one crystal was not unusual. One end of the main tube was ground off and closed by a glass plate waxed on with ordinary red sealing wax, care being taken to keep the wax on the outside of the tube. Contamination by grease vapors was thus entirely eliminated and that by vapors of wax reduced to a very small amount.

Originally a small Faraday cylinder was used as a collector. It was found that the measured ion current to such a cylinder was sensibly the same no matter whether the ions struck the inside of the cylinder or the bottom outside. It has been noted by others[8] that the reflection of positive ions almost disappears at normal incidence. Furthermore, a particularly clean surface seems to be necessary to secure much reflection at any angle, and no pains were taken to secure this degree of cleanliness of the collector. Hence, since the ions would be incident normal to the collector and the collector was not especially cleaned, one would not expect loss of ions by reflection even from a simple strip. Experience bears out this conclusion. The cylinder was later replaced by a strip because it took up less space.

Method

The accelerating potential could be applied in two parts: one between the source and the drum, the other between the cylinder and the reflector, drum and cylinder both being grounded. The field between cylinder and reflector served both to accelerate primary ions moving toward the reflector and to retard reflected ions leaving it. Thus by making the source 30 volts positive and the reflector 20 volts negative with respect to the drum and cylinder, the ions caught by the collector would have struck the reflector with an energy of 50 volts and would have retained 20 volts or more after impact. These will be designated as 50–20 volt ions.

It is true that with this arrangement the ions are in a field of force while they are being reflected and this may conceivably influence the reflection somewhat. The geometry of the tube was such that the field between the cylinder and the reflector was, to a rough approximation, radial, and the velocities of the reflected ions should not have been greatly altered by it as regards direction. Furthermore, when a reading was being taken the field around the cylinder was not distorted by the presence of the collector, since its potential at such a time was always zero. One disadvantage of this method is that the field between the cylinder and the reflector focuses the incident beam to some extent, so that even though the ion current getting through the holes in the drum remains constant, the number of ions striking the reflector is greater the greater the potential difference between it and the cylinder. Thus for the higher retarding potentials, i.e., larger fractions of total accelerating potential applied between cylinder and reflector, the current to the reflector is actually increased.

[8] Gurney, reference 2, p. 472, and his quotation of Jackson, Phys. Rev. **28,** 524 (1926).

An alternative method would be to keep the drum, cylinder, and reflector all at ground potential, applying the whole accelerating field between the source and the drum, and the retarding field between the cylinder and collector. This has two disadvantages. In the first place, the field in the immediate vicinity of the collector tends to change the direction of approaching ions, deflecting them so that some which should strike the collector now miss it entirely. In the second place, this method involves placing the whole collector-electrometer system at a positive potential, sometimes comparatively high, with the consequently greater likelihood of insulation leaks. All of the data in this paper were obtained with the first arrangement.

The procedure in taking a series of readings was as follows. The desired accelerating and retarding potentials were applied and the source was heated for several minutes until the emission became steady. The total ion current getting through the holes in the drum was measured by turning the collector so as to cover the holes. This current was kept as nearly constant as possible and was checked occasionally during a run, little difficulty being found in maintaining constancy. The heating current through the reflector was adjusted to give the desired temperature and the collector then rotated so as to collect ions reflected at various angles. The width of the collector subtended an angle of about 9.5° at the center of the reflector, and in taking readings settings were made at 10° intervals. The pressure was kept as low as possible, being of the order of 10^{-6} mm. If the reflector were at any temperature higher than that of a just visible red heat, it was found necessary to apply to it a negative potential of 2 or 3 volts in order to suppress positive ion emission from the reflector itself.

Results

In general, the reflector gave more intense reflection when hot than when cold, though little change was observed as the temperature was raised beyond a medium red. In most of the following work a medium red heat was used. It is probable, as Read and Gurney suggested, that the increased reflection when hot was due to the removal of surface films of gas or grease. Read reported that within a few seconds after the heating current was turned off no reflection could be detected, while Gurney publishes a curve showing that the intensity of reflection decreased to 0.4 of its initial value during the first minute after heating was stopped. With the tube used in this investigation it was found that the intensity was 0.9 of its original value after an interval of 8 minutes, in one instance, and even after 20 minutes it had sunk only to 0.86 I_0.

When only small retarding fields were applied so that ions of all but the very lowest velocities were collected, reflection was found as shown in Figs. 3–6. The figures show the incident beam coming from the right, and the length of the radius vector from the center of the reflector to any point on a curve is proportional to the intensity of reflection at that angle. The broken lines marked N and S show, respectively, the normal to the surface and the angle of specular reflection.

The reflection from platinum, Fig. 3, shows much the same sort of distribution as reported by Read and Gurney, but there are several points of difference. Apparently there was considerably more diffuse scattering at small

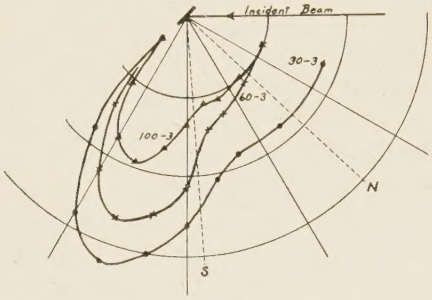


Fig. 3. Reflection from platinum, angle of incidence 43°. Small retarding potentials.

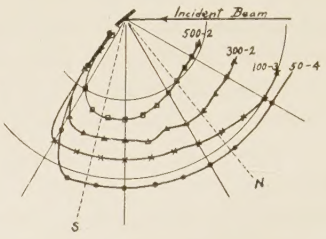


Fig. 4. Reflection from nickel, angle of incidence 51.5°. Small retarding potentials.

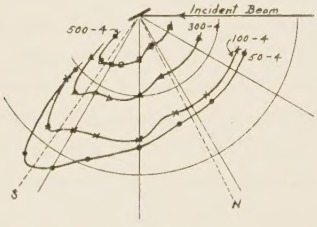


Fig. 5. Reflection from nickel, angle of incidence 62.5°. Small retarding potentials.

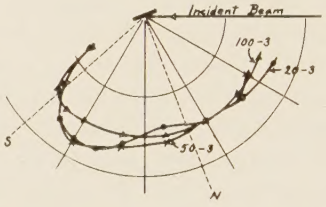


Fig. 6. Reflection from nickel, angle of incidence 69°. Small retarding potentials.

angles than was found by either Read or Gurney. There is a rather broad peak in each curve, the maximum falling at a larger angle than specular reflection would give. Contrary to the findings of Read, the position of this maximum did not change with a change in the accelerating potential.

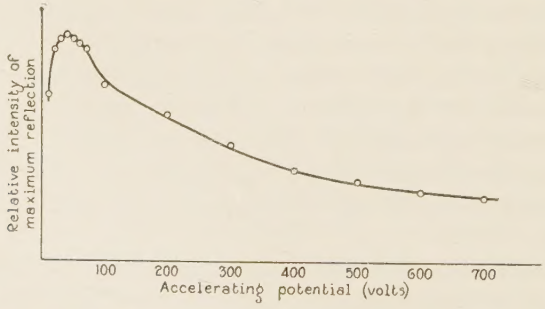


Fig. 7. Reflection from nickel, angle of incidence 62.5°.

The curves for a nickel crystal reflector, Figs. 4–6, show hardly any peaks in some cases. Where they do occur they are not as prominent as with the platinum reflector, and fall much more nearly at the specular angle.

The relation between the intensity of the maximum and the accelerating potential is shown in Fig. 7 for a nickel reflector with a primary beam incident at 62.5°. The maximum in the neighborhood of 40 volts agrees with the results of Read and Gurney for platinum.

Figs. 8–13 are curves for larger retarding potentials. These curves show directly the angular distribution of all reflected ions having more than a certain amount of energy. For instance, the 50–20 volt curve of Fig. 8 shows the distribution of ions which originally had an energy of 50 volts and which retained 20 volts or more after reflection. For low accelerating potentials these curves show a progressive shift of the maximum toward larger angles as the retarding potential is increased, indicated in Fig. 8. This shows that the ions which were the least deviated from their original directions were apt to have higher velocities than those which were deflected through larger angles. This corroborates the result obtained by Gurney.

From a set of curves such as Fig. 8 or Fig. 9 it is possible to get some idea of the velocity distribution of the ions as well as their distribution in angle.

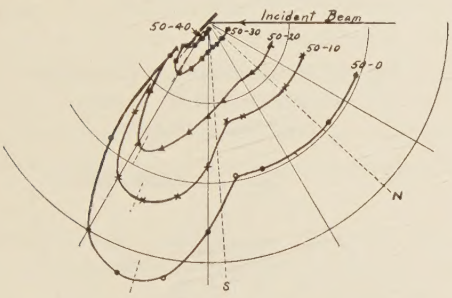


Fig. 8. Reflection from platinum, angle of incidence 43°. Large retarding potentials.

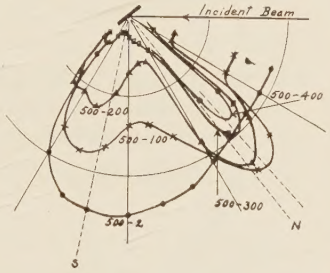


Fig. 9. Reflection from nickel, angle of incidence 51.5°. Large retarding potentials.

Thus in Fig. 9 it is seen that there is a fairly well-defined beam of ions coming off at an angle just inside the normal to the surface, and the ions composing the beam seem to have retained a large part of their original energy. The fact that some of the curves for large retarding potentials show a greater intensity than those for smaller retarding potentials at a given angle may be explained by the focusing effect of the field between the cylinder and the reflector, as before mentioned. Increasing the retarding potential accentuates the specularly reflected peak, though reducing its intensity, at the same time bringing into marked prominence the high velocity beam which must previously have been obscured by general, low velocity scattering. It should be noted that the position of this new peak, as shown in Figs. 10–13, is unaffected by a change in the accelerating potential of the incident ions up to 700 volts, the largest used. This is not particularly apparent in Fig. 11. While the number of voltages used for an angle of incidence of 62.5° was not as large as might be desirable to locate accurately the position of the new peak, careful examination of all the data taken leads to the conclusion that the maximum was located at about 5° inside the normal, as shown by the 250–150 volt curve.

However, the accuracy of measurement was hardly sufficient to locate the maximum within 5°.

The peak near the normal was not observed with accelerating voltages below 200 volts and increased in prominence as the accelerating potential was raised. Its position so near the normal to the surface at once suggested that it might be due to the condensation of ions upon the surface and their subsequent evaporation, according to the theory of Langmuir[9] and Frenkel.[10] This would result in a cosine distribution with a maximum along the normal. However, it would hardly be expected that the ions would evaporate with such high velocities as were observed, if, indeed, they evaporated as ions at

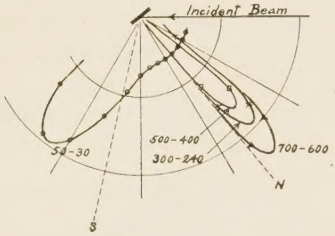


Fig. 10. Reflection from nickel, angle of incidence 51.5°. Large retarding potentials.

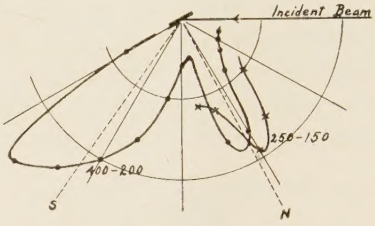


Fig. 11. Reflection from nickel, angle of incidence 62.5°. Large retarding potentials.

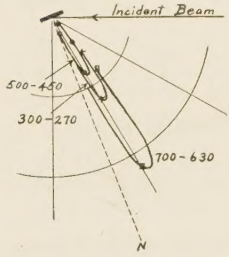


Fig. 12. Reflection from nickel, angle of incidence 69°. Large retarding potentials.

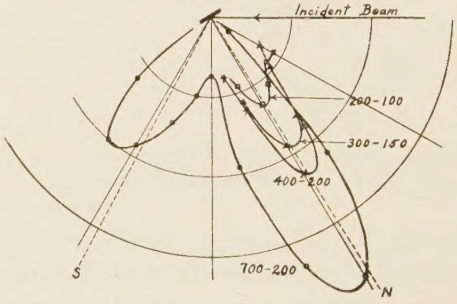


Fig. 13. Reflection from platinum, angle of incidence 59°. Large retarding potentials.

all. The sharpness of the peak, too, did not suggest a cosine law. As a further check on the adsorption—re-evaporation idea, the effect was tried of changing the density of the ion stream, since the work of Cockcroft[11] indicated that stream density was an important factor in molecular condensation. However, it seemed to be impossible to make the peak either appear or disappear simply by changing the ion current. In one trial, using a voltage below that at which the peak appeared, an increase in the current by a factor of thirty failed to produce a peak.

A hot reflector gave the effect better than a cold one. It was not observed

[9] Langmuir, Phys. Rev. **8**, 149 (1916).
[10] Frenkel, Zeits. f. Physik **26**, 117 (1924).
[11] Cockcroft, Proc. Roy. Soc. **A119**, 293 (1928).

at all with a nickel crystal reflector at an angle of incidence of 42° or with platinum at 44°.

When the larger accelerating potentials were used there sometimes appeared to be an emission of secondary electrons from the reflector. It was usually possible, by the application of a suitable magnetic field, to prevent these from reaching the collector and yet to leave the positive ions practically unaffected.

Discussion

The reflected beam of ions coming off near the normal to the surface and having nearly the same velocity as the incident ions is the most interesting result of this study. It would be most natural to try to attribute it to positive ion diffraction were it not for the fact that the position of the beam is independent of the accelerating potential. The wave-length associated with a 200 volt lithium ion would be expected to be approximately 0.01A. Although it is difficult to predict the behavior to be expected of a complex ion when it strikes a crystal surface, specular reflection would seem to be as likely as anything else. A consideration of the possibilities of such reflection from various planes in the nickel crystals shows that, of those having the largest atom densities, only the (110) planes could give specular reflection at approximately the observed angles. Table I shows the angles observed and calculated. Having no accurate knowledge of the crystal structure of the platinum reflector, it is impossible to calculate the reflection as in the case of the nickel crystals.

Table I. *Reflection from nickel crystals. All angles measured from the normal to the surface.*

Angle of incience on (111) planes	Angle of Reflection Calculated from (110) planes	Observed	Difference
51.5°	19.5°	8.5°	+11.0°
62.5°	8.5°	5.5°	+3.0°
69.0°	2.0°	9.0°	−7.0°

One argument against the hypothesis of reflection by the (110) planes is that the differences between observed and calculated values of the angles show a systematic trend in one direction. However, the number of different angles tried was not sufficient to permit drawing a definite conclusion. The reflected beam was so nearly normal to the surface as to suggest the possibility that more accurate measurements might show it to lie exactly along that direction. A rough test of the relative satisfactoriness of the two suppositions—reflection by the (110) planes or reflection along the normal—is found by applying the method of least squares, though here again a greater number of angles would be desirable. This method gives little choice between the two hypotheses, the slight difference being in favor of the first mentioned.

The writer wishes to acknowledge his indebtedness and express his appreciation to Professor A. J. Dempster, who proposed the problem and whose suggestions proved extremely valuable, and to Mr. K. S. Woodcock, who assisted in taking some of the data and making the drawings.